

COLOUR AND CHEMICAL CONSTITUTION.

PART XI.—A SYSTEMATIC STUDY OF THE BROMINATED PHENOLPHTHALEINS
REGARDING THE RELATION BETWEEN POSITION AND COLOUR.

BY JAMES MOIR.

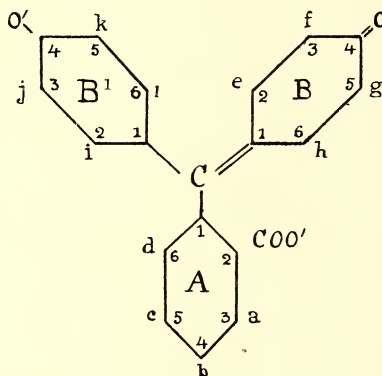
In Part IX of this work a mathematical formula was developed whereby the colour of any halogenated phenolphthalein could be calculated. The application of this formula was, however, in practice limited to substances halogenated in the phenol rings, it being known that the four phthalic positions are very abnormal (although the four taken together are very nearly equivalent to four phenolic positions).

The formula when confined to the halogen bromine alone reads $\frac{\lambda_0}{\lambda} = 1 - 0.0128m$, or since in phenolphthalein $\lambda_0 = 554$, $\lambda = \frac{554}{1 - 0.0128m}$, in which m is the number of (ortho) bromine atoms present in the brominated phenolphthalein the colour of which is to be calculated. For meta-bromine atoms m is to be doubled. The expression $\frac{554}{1 - 0.0128m}$ can for simplicity be written without a divisor as $554 (1 + 0.0128m + 0.000164m^2)$, hence finally $\lambda = 554 + 7.091m + 0.091m^2$. Terms containing higher powers of m are negligible.

Hence if m is a small number, less than 5, the wave-length may be taken to be $7\frac{1}{2}$ units higher than 554 for each ortho-bromine atom present. Thus 561 $\frac{1}{2}$, 569, 576 $\frac{1}{2}$ and 584 are the wave-lengths of (ortho) mono-, di-, tri- and tetra-bromophenolphthalein. This, though not strictly accurate, agrees with observation within one unit.

I have, however, shown in Part II (foot of p. 113) that substitution of a second phenolic ring produces less effect than substitution of the first ring, the latter producing about 58 per cent (or four-sevenths) of the effect of substituting both phenolic rings, and the former 42 per cent. (or three-sevenths) of the effect.

I have now completed the study of the effect of bromine on colour by preparing the phthaleins derived from the brominated phthalic acids, and am now able to give a tabular statement showing how the position of the bromine atoms affects the colour, and enabling that of any polybromoderivative to be calculated, since the property is additive.



Systematic nomenclature of the positions in alkaline phenolphthalein.

Table giving Value in Colour-change of a Bromine-atom in the Different Substituting Positions.

Position	<i>b</i> or A4	has value	1
"	<i>j</i>	" B'3	7
"	<i>k</i>	" B'5	7
"	<i>c</i>	" A5	8
"	<i>f</i>	" B3	8
"	<i>g</i>	" B5	8
"	<i>a</i>	" A3	10
"	<i>d</i>	" A6	10
"	<i>i</i>	" B'2	13
"	<i>l</i>	" B'6	13
"	<i>e</i>	" B2	15
"	<i>h</i>	" B6	15

NOTE.—These values are to be added to 554 to get the wave-length of the absorption of the brominated phenolphthalein.

The unit is 1 in the third place of wave-lengths = 10 Angstrom units.
The positions are not in alphabetical order, but in order of magnitude.

It is to be noted, however, that the difference between the positions *f*, *g*, *j* and *k* does not come into play unless there is substitution in *both* rings B and B': thus there is only one mono-orthobromphenolphthalein, which I

assume to be the *f* or *g* derivative, not the *j* or *k* derivative: the same holds of the positions *e*, *h*, *i* and *l*, there being only one mono-metabromphenolphthalein. On inspection of the figure it will be seen that only five distinct monobromphenolphthaleins are to be expected, or at all events, although six are possible (*a*, *b*, *c*, *d*, *e* and *f*), yet the *a* and the *d* derivatives either have the same spectrum or are never formed together when 3-bromophthalic acid is condensed with phenol (this might be expected owing to "protection," which would prevent the formation of the *d* derivative).

Monobromophenolphthaleins.

Position of bromine atom.	Method of formation.	Observed band-centre.	Calculated from position-law.
<i>a</i>	3-bromophthalic acid and phenol	λ 566	λ 564
<i>b</i>	Bye-product of <i>c</i>	λ 556*	λ 555
<i>c</i>	4-bromophthalic acid and phenol	λ 561*	λ 562
<i>e</i>	OBBA† and monometabromphenol	λ 567	λ 569
<i>f</i>	OBBA† and mono-orthobromphenol	λ 561½	λ 562

* Imperfectly separated.

† OBBA = 4-oxybenzoylbenzoic acid.

For comparison with the first of these, *a*-monochlorphenolphthalein was made. Its band-centre was at λ 563.

As regards the dibromophenolphthaleins, there appear to be 21 possible isomers, viz.: (1) *a-d* from 3-6-dibromphthalic acid; (2) *b-c* from 4-5-dibromphthalic acid; (3) *a-b* and (4) *c-d* from 3-4-dibromphthalic acid; (5) *a-c* and (6) *b-d* from 3-5-dibromphthalic acid; (7) *a-e* and (8) *d-e* from 3-(6)-bromo-4'-oxybenzophenone-2-carboxylic acid and metabromphenol; (9) *b-e* and (10) *c-e* from the isomeric 4-(5)-bromo acid; (11) *a-f* and (12) *d-f* from the former acid and orthobromphenol; (13) *b-f* and (14) *c-f* from the isomeric 4-bromo-4'-oxybenzophenone-2-carboxylic acid and orthobromphenol; (15) *e-f* from OBBA† and 2-3-dibromphenol; (16) *e-g* similarly from 2-5-dibromphenol; (17) *e-h* similarly from 3-5-dibromphenol; (18) *f-g* similarly from 2-6-dibromphenol; (19) *e-i* from phthalic acid and 2 mols. metabromphenol; (20) *f-j* from phthalic acid and 2 mols. orthobromphenol; and finally (21) *e-j* by condensing phthalic acid first with orthobromphenol and then with metabromphenol.

Of these 21 isomers, 4 may be eliminated if we assume that the colour-effect of the *d*-position is the same as that of the *a*-position; these 4 are *b-d*, *c-d*, *d-e* and *d-f*. Of the 17 remaining I have, of course, only been able to prepare and examine a very few, owing to lack of starting-substances in South Africa, and the following table exhibits the results obtained:

Dibromophenolphthaleins.

Position of bromine atoms.	Method of formation.	Observed band-centre.	Calculated from position-law.
<i>a-d</i>	3-6-dibromphthalic acid <i>ex</i> 1-4-dibromnaphthalene	λ 573	λ 574
<i>b-c</i> (?)	4-5 (?) dibromphthalic acid <i>ex</i> silver phthalate + 2Br ₂	λ 564	λ 563
<i>a-c</i>	3-5 dibromphthalic acid <i>ex</i> anthranilic acid	λ 571	λ 572
<i>f-g</i>	OBBA and 2-6-dibromphenol	λ 570	λ 570
<i>f-j</i>	Phthalic acid and 2-bromophenol	λ 569	λ 569

The number of tribromophenolphthaleins possible is much larger, viz. 54, but if, as suggested above, those which contain the *d*-position and not the *a*-position be eliminated, there remain 42 possible different spectra for the isomers. It will be sufficient to enumerate these, since their method of formation is obvious by what has gone before. They are:

<i>a-b-c</i>	<i>a-d-f</i>	<i>a-e-i</i>	<i>b-e-i</i>	<i>c-e-i</i>	<i>e-f-j</i>
<i>a-b-d</i>	<i>b-c-f</i>	<i>a-e-j</i>	<i>b-e-j</i>	<i>c-e-j</i>	<i>e-g-i</i>
<i>a-c-d</i>	<i>a-c-f</i>	<i>a-f-g</i>	<i>b-f-g</i>	<i>c-f-g</i>	<i>e-g-j</i>
<i>a-d-e</i>	<i>a-b-f</i>	<i>a-f-j</i>	<i>b-f-j</i>	<i>c-f-j</i>	<i>e-h-i</i>
<i>b-c-e</i>	<i>a-e-f</i>	<i>b-e-f</i>	<i>c-e-f</i>	<i>e-f-g</i>	<i>e-h-j</i>
<i>a-c-e</i>	<i>a-e-g</i>	<i>b-e-g</i>	<i>c-e-g</i>	<i>e-f-h</i>	<i>e-j-k</i>
<i>a-b-e</i>	<i>a-e-h</i>	<i>b-e-h</i>	<i>c-e-h</i>	<i>e-f-i</i>	<i>f-g-j</i>

Tribromophenolphthaleins.

Position of bromine atoms.	Method of formation.	Observed band-centre.	Calculated from position-law.
<i>a-b-d</i> <i>a-c-d</i>	3-4 (or 5)-6-tribromophthalic acid and phenol Dibromo derivative of OBBA and orthobromphenol	} 576 inseparable 577	{ 575 582 577
<i>f-g-j</i>			

Only these two could be prepared. In all the other cases tried the reaction went abnormally, giving substances which from the behaviour of phenolphthalein when heated with conc. H₂SO₄, and from their spectra, may be identified as isomeric varieties of dibromoxanthraquinone.

There appear to be 80 possibilities for tetrabromophenolphthalein if the *d*-position is not counted unless the *a*-position is present. The first 7 are *abcd*, *abce*, *abcf*, *abde*, *abdf*, *acde* and *acdf*; then follow 28 made by combining the series *ef*, *eg*, *eh*, *ei*, *ej*, *fg*, *fh* with the series *ab*, *ac*, *ad*, *bc*; then follow 30 made by combining the series *efg*, *efh*, *efi*, *efj*, *egi*, *ehi*, *egj*, *ehj*, *fgi*, *fgj* successively with *a*, *b* and *c*. The remainder are *efg* combined with *h*, *i*, *j*;

efhi and *efhj*; *efi* combined with *j*, *k* and *l*; *egi* with *k* and *l* and *ehil*; and finally *fgij*, *fgik*, *fgil* and *fgjk*. Of this multitude of isomers only two could be prepared, viz.:

Tetrabromophenolphthaleins.

Position of bromine atoms.	Method of formation.	Observed band-centre.	Calculated from position-law.
<i>a-b-c-d</i> <i>f-g-j-k</i>	Tetrabromophthalic acid and phenol Dibromo-OBBA and 2-6-dibromophenol, also by bromination of phenolphthalein	λ 583* λ 584	λ 583 λ 584

* The figures given in Part I, 1917, of this work for this substance and the thymol derivative are erroneous.

Taking account of the foregoing convention about the *d*-position, I find that the number of possible pentabromophenolphthaleins is 118. I have made and observed only those which are derived from the mono-derivatives by perbromination.

Pentabromophenolphthaleins.

Position of bromine atoms.	Source.	Observed band-centre.	Calculated from position-law.
<i>a-f-g-j-k</i> <i>b (or c)-f-g-j-k</i> <i>e-f-g-j-k</i>	<i>a</i> -monobromophenolphthalein 4-bromophthalic acid + phenol + bromine <i>e</i> -monobromophenolphthalein	λ 597 } λ 592 λ 602	λ 594 $\lambda\lambda$ { 585 <i>b</i> 592 <i>c</i> λ 599

As regards the hexabromophenolphthaleins, the possible number is 134, taking account of the convention. Again I have only observed those obtainable by perbromination of lower brominated substances.

Hexabromophenolphthaleins.

Position of bromine atoms.	Source.	Observed band-centre.	Calculated from position-law.
<i>a-d-f-g-j-k</i> <i>a-c-f-g-j-k</i> <i>b-c (?) -f-g-j-k</i> <i>c (?) -e (?) -f-g-j-k</i>	<i>a-d</i> -dibromophenolphthalein <i>a-c</i> -dibromophenolphthalein 3rd dibromo-compound Bromine on ordinary tetrabromo-compound*	λ 606 λ 602 λ 592 λ 605	λ 604 λ 602 λ 593 λ 607

* Only a trace obtained.

Heptabromophenolphthaleins.

Position of bromine atoms.	Source.	Observed band-centre.	Calculated from position-law.
<i>a-b (?) -d-f-g-j-k</i>	Tribromo-compound	λ 609 vague	$\left\{ \begin{array}{l} \lambda \text{ 605 } b \\ \lambda \text{ 612 } c \end{array} \right.$

The possible number is the same as that of the penta-derivatives, viz. 118. The possible number of octobromo-compounds is the same as that of the tetra-compounds, viz. 80, and so on with the nono-, deca- and hendeca-compounds. The substance *a-b-c-d-f-g-j-k* has been made in America, but I find it difficult to make a perfectly pure preparation. The figure given in Part I of this work, viz. λ 608, is certainly too low, since its band-centre should be at λ 613 or λ 614 by calculation.

A perchloro-derivative of phenolphthalein has been mentioned in Part IX, and is green in alkali with band-centre λ 642. The corresponding bromo-compound would have its band-centre at about λ 647.* The theory for a decabromophenolphthalein having all the positions except *a* and *d* occupied is λ 649, and it is reasonable to assume, from the analogy of phthalic acid, that the *a*- and *d*-positions would not be attacked by chlorine at the low temperature of boiling CHCl_3 . This green substance is therefore *bcefg hijkl*-decachlorophenolphthalein.

Another chlorine derivative which is new is monometachlorophenolphthalein, made from OBBA and metachlorphenol with H_2SO_4 at 100°C . Its band-centre was found to be at λ 564 only, and the band was broad. The theoretical figure is λ 568 $\frac{1}{2}$, and it is possible that the substance was contaminated with *o-p*-phenolphthalein, λ 559, arising from the OBBA alone. It is not possible to distinguish two band-centres unless they are at least 7 units in λ apart.

The corresponding monometaiodophenolphthalein was made in an analogous manner. Its band in alkali was at first broad, but on standing became narrow at λ 568 $\frac{1}{2}$ (theory 569 $\frac{1}{2}$). This substance was next perbrominated, and the penta-derivative (*f-g-j-k*-tetrabromo-*e*-iodophenolphthalein) was found to have λ 600, which agrees with theory ($554 + 30 + 15\frac{1}{2}$).

A penta-iodo-phenolphthalein was obtained by treating the barium salt of phenolphthalein with excess of warm solution of iodine in KI. Its band-centre was at λ 596, which differs from that of the *f-g-j-k*-tetriodo-compound (which is first formed) by 10 units. I infer, since iodination in the *a*-position

* From the law given in Part IX.

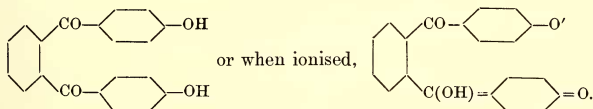
is very unlikely, that this substance is a mixture of the isomers *e-f-g-j-k* and *c-f-g-j-k* (theories λ 601 and λ 594).

Constitution of Phenolphthalein.

Having now exhibited the experimental evidence, I ask the reader to examine again the table on p. 130, which has been constructed from this evidence, and, confining his attention to the phthalic ring, particularly the positions *b* and *c*, to remember the result obtained in the study of benzaurine-derivatives (Part X). The latter were found to have a *negative* para-position: thus aurine, which is parahydroxybenzaurine, has λ 534, as against λ 553 for benzaurine; so the paracarboxylic acid of benzaurine (*ex* terephthalic acid and phenol) has λ 550, again showing a lowering caused by the para-position, its isomer, phenolphthalein having λ 554. Now, as the table on p. 130 shows, this lowering does not occur when phenolphthalein is substituted in the para-position, when *b*-monobromophenolphthalein would have had λ 546 instead of λ 556 (colour-value = - 8 instead of + 1).

I infer from this therefore that the customary formulation of phenolphthalein (that on p. 130) is not the correct one. This formulation makes phenolphthalein to be simply the ortho- or A2-carboxylic acid of benzaurine, which, if true, should cause it to have a negative para-position as regards colour. In this connection also I may repeat what I have said before—that if phenolphthalein were really benzaurine-A2-carboxylic acid, it ought to exhibit the yellow colour of benzaurine derivatives when its alkaline solution is carefully neutralised (and then pass into a colourless lactone). Both phenoltterephthalein and phenolsulphonephthalein change from pink to yellow on neutralising, and they are undoubtedly derivatives of benzaurine.

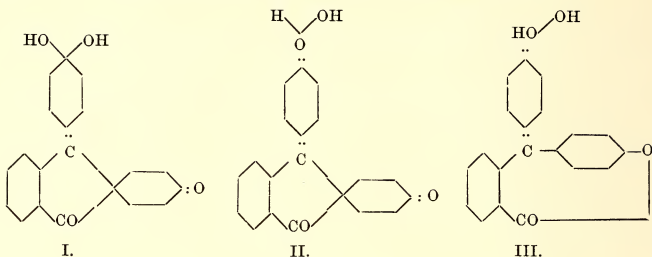
The customary formula for alkaline phenolphthalein, which has been accepted for thirty-five years, having been shown to be unsatisfactory, we may next consider the one which was current before 1885, viz :



Phenolphthalein was then known as dioxypthalophenone.

Now these formulæ were rejected about 1885 when it was discovered that diphenylphthalide had both phenyl rings on the same carbon-atom, and it was assumed, in some manner which I am unable to trace, that phenolphthalein is the dioxo-derivative of diphenylphthalide.

I should like therefore to put forward tentatively some of the other possible schemes, *e. g.* :



These are combinations of the two former ideas, and depict phenolphthalein both as benzaurine-derivative and as a phthalophenone. They explain the easy formation of an oxime, and the easy change of the latter into oxybenzoylbenzoic acid and para-aminophenol.

I should add, of course, that I have no doubt that solid colourless phenolphthalein has the accepted lactone formula; the only question that is in doubt is the constitution of its coloured solutions in alkali, and I am fairly confident that the latter do not contain a free $-\text{CO}_2\text{Na}$ (or $-\text{CO}_2'$ ion), but are wholly phenolic in their character. The same applies to fluorescein, which may turn out to be merely an oxo-dioxyphthalophenone when in alkaline solution, although a triphenylcarbinol-derivative when solid.